Catalyst Additives to Enhance Mercury Oxidation and Capture

Quarterly Report

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Abstract

Preliminary research has shown that SCR catalysts employed for nitrogen-oxide reduction can effectively oxidize mercury. This report discusses initial results from fundamental investigations into the behavior of mercury species in the presence of SCR catalysts at Southern Research Institute. Three different SCR catalysts are being studied. These are honeycomb-type, plate-type, and a hybrid-type catalyst. The catalysts are manufactured and supplied by Cormetech Inc., Hitachi America Ltd., and Haldor-Topsoe Inc., respectively. Test methods and experimental procedures were developed for current and future testing. The methods and procedures equalize factors influencing mercury adsorption and oxidation (surface area, catalyst activity, and pore structure) that normally differ for each catalyst type. Initial testing was performed to determine the time necessary for each catalyst to reach surface-adsorption equilibrium. In addition, the fraction of Hg oxidized by each of the SCR catalyst types is being investigated, for a given amount of catalyst and flow rate of mercury and flue gas. The next major effort will be to examine the kinetics of mercury oxidation across the SCR catalysts with respect to changes in mercury concentration and with respect to HCl concentration. Hg-sorption equilibrium times will also be investigated with respect to ammonia concentration in the simulated flue gas.

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Introduction

The objective of this project proposed by Southern Research Institute (Southern Research) is to investigate the enhancement of elemental-mercury oxidation in coal-fired flue gas through catalysis. In addition to testing various catalyst materials, fundamental mechanisms associated with enhanced Hg-oxidation on SCR catalysts are being investigated. Data obtained in this work will be provided to Niksa Energy Associates (NES) and Reaction Engineering International (REI) to develop and improve models to predict mercury speciation in full-scale boilers, burning different coal types, ranging from sub-bituminous to high-volatile bituminous coals. Where necessary, Southern Research will develop semi-empirical mechanistic model(s) describing the mechanisms associated with catalysis enhanced mercury oxidation. Results from the project will contribute to a greater understanding of mercury oxidation in flue gas.

Executive Summary

Southern Research Institute conducted bench-scale reactor studies in the last quarter of 2004 to evaluate the behavior of vapor-phase mercury in the presence of Selective Catalytic Reduction (SCR) catalysts. SCR catalysts are employed in coal-fired power plants for the reduction of nitrogen oxide (NO_x) emissions, but SCR catalysts also affect the speciation of other gases, such as mercury. Mercury primarily exists in two-different forms in coal-derived flue gas, $HgCl_2$ and the elemental form, and each type behaves somewhat differently in the "back end" pollution control equipment of power plants. Oxidized mercury is readily captured in some of the commonly employed pollution control devices, such as wet scrubbers, while elemental mercury is much harder to capture. Therefore, a low-cost mercury-oxidation technology is desired for coal-fired power plants. The best option would be a multi-pollutant solution, such as SCR catalysts for NO_x reduction and mercury oxidation.

The Catalyst Test Facility (CTF) continues to be used to derive fundamental kinetic information about each catalyst and catalyst material investigated for mercury oxidation and capture. All of the materials tested during the last quarter of 2004 were commercially offered SCR catalysts. The CTF is described and illustrated in this quarterly report. At the core of the CTF is an extensive flue-gas simulation, gas flow, and metering system. Catalyst samples are supported in a 1-½" square (for honeycomb-type and hybrid catalysts) or 1-¼" x 2" rectangular (for plate-type) pyrex reactor, through which the entire gas flow must pass. The CTF simulates clean (no particles) flue gas with all the major flue-gas species present, including CO, CO_2, H_2O, O_2, N_2, HCl, NO, SO_2, SO_3, and Hg°, in concentrations representative of that found in flue gases of existing power plants, burning specific coal types.

The simulated flue gas originates from compressed-gas cylinders. The gases from the cylinders are then mixed to known concentrations by use of precision mass-flow controllers. The appropriate moisture content is generated through precise control of water evaporation. Mercury is added to the system via a mercury-soaked porous-ceramic tube within an excess-volume chamber. The simulated flue-gas stream is well mixed and preheated before entering the reaction chamber. A 3"-diameter by 3'-long tube furnace heats the reactor, which allows the simulated flue gas to pass through the furnace while holding the catalyst samples in place.

Bench-scale SCR catalyst tests were conducted to elucidate the relationship between the SCR catalysts and mercury speciation under particular flue-gas environments. The procedure and basis for normalizing mercury adsorption and oxidation, in order for all three catalyst types

to be compared on an equal basis, is described. The applicable temperature range of these experiments was chosen from typical operating temperatures of actual SCR reactor installations, and is from 650 °F to 750 °F. The only simulated flue-gas type tested on SCR catalysts thus far has been for a low-NO_x power plant burning Powder River Basin (PRB) coal, though SCR catalyst tests using other flue gas types are planned.

Next quarter, experiments similar to those described in this report will continue to be performed. The kinetic rate for mercury adsorption by each catalyst will be determined. Also, the impact of varied partial pressures of ammonia will be investigated. Fundamental rates and mechanisms of mercury sorption and oxidation on SCR catalysts will be elucidated from the results of these experiments.

Experimental

Figures 1-3 show pictures of the CTF's quartz furnace (micro-reactor), gas-conditioning bubblers for mercury speciation and stabilization prior to mercury monitoring, flue-gas continuous emission monitors (CEMs), and gas-flow control systems. Both elemental and total mercury are measured at the outlet of the CTF.

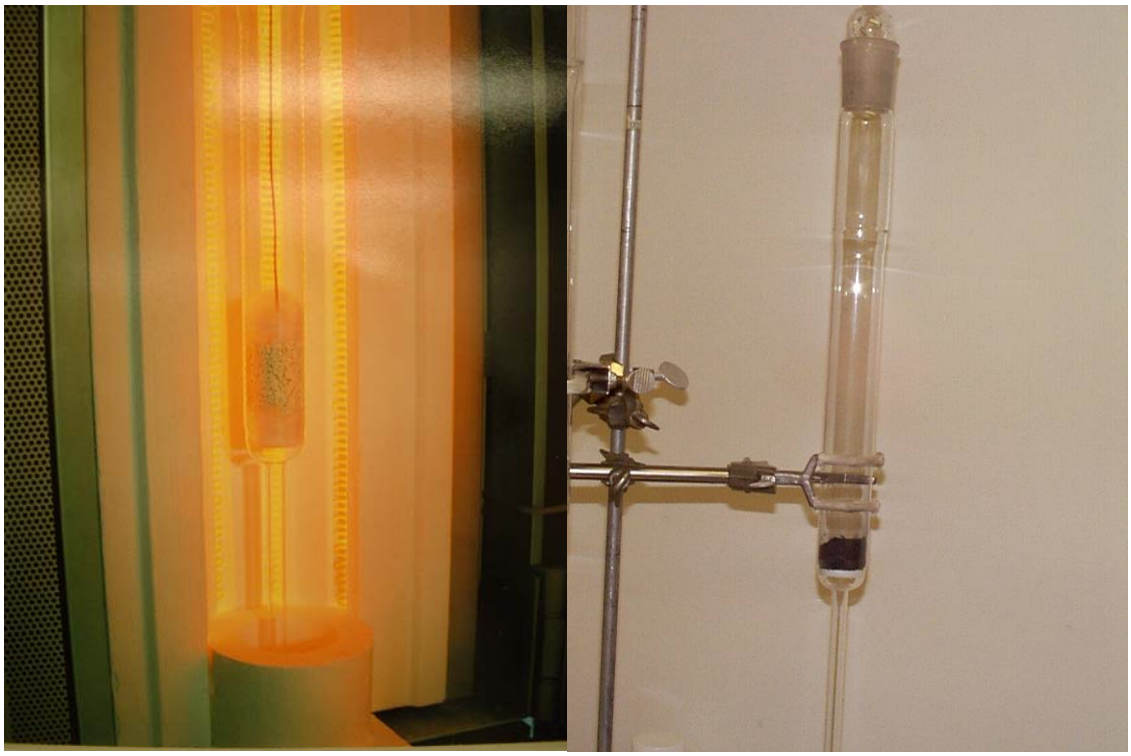

Figure 1. CTF quartz furnace at ~1000 °C (left) and outside of furnace (right).

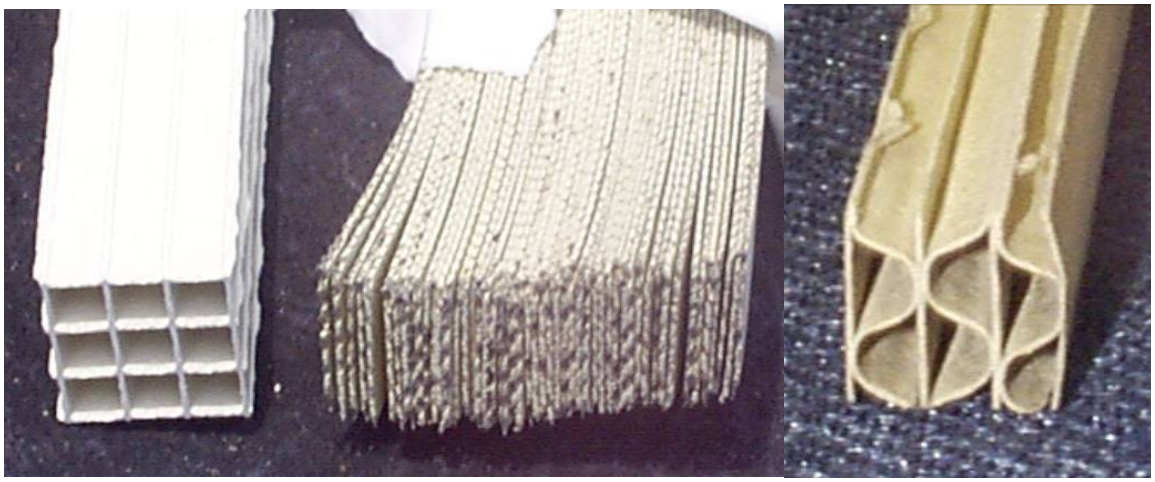

Figure 2. From left to right, honeycomb, plate, and hybrid SCR catalysts.

The CTF simulates clean (no particles) flue gas with all the major flue-gas species present, including CO, CO_2, H_2O, O_2, N_2, HCl, NO_x, SO_2, SO_3, and Hg°, in concentrations that exist in the flue gases of existing power plants, burning specific coal types. The simulated flue gas is originated from compressed-gas cylinders. The gases from the cylinders are then mixed to known concentrations by use of mass flow controllers. The appropriate moisture content is generated through precise control of water evaporation. Mercury is added to the system via a mercury-soaked porous-ceramic tube within an excess-volume chamber. The simulated flue-gas stream is well mixed and preheated before entering the reaction chamber. A 3"-diameter by 3'-long tube furnace heats the reactor, which allows the simulated flue gas to pass through the furnace while holding the catalyst samples in place. The three different catalyst samples are shown in Figure 2.

The majority (i.e., over 95%) of NOx in the flue gas of coal-fired boiler systems is in the forms of NO. Hence, NO is generally used in this work to simulate the NOx in the flue gas, except for experiments specifically conducted to observe the effect of NO2. In such case, mixed NO/NO2 gas bottles will be used to simulate the NOx in the flue gas. With only NO in the flue gas, the NOx reduction reaction is simplified to the following:

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \qquad (1)$$

All heated sections of the micro-reactor within the CTF system are made of quartz glass to limit side reactions that might occur as a result of wall effects. A semi-continuous emission monitor (SCEM) is employed to detect the mercury levels exiting the reaction chamber. A gas-conditioning system is used to convert all Hg into the elemental form, for detection using a combined gold-trap and atomic fluorescence monitor. A Tekran Model 2573A Mercury Vapor Analyzer is used to detect the elemental mercury. Along with mercury, simultaneous measurements of oxygen, carbon dioxide, nitrogen oxides, and sulfur dioxide are made using continuous emission monitors. Figure 4 shows a schematic of the CTF system layout.

Figure 3. Catalyst Test Facility**.**

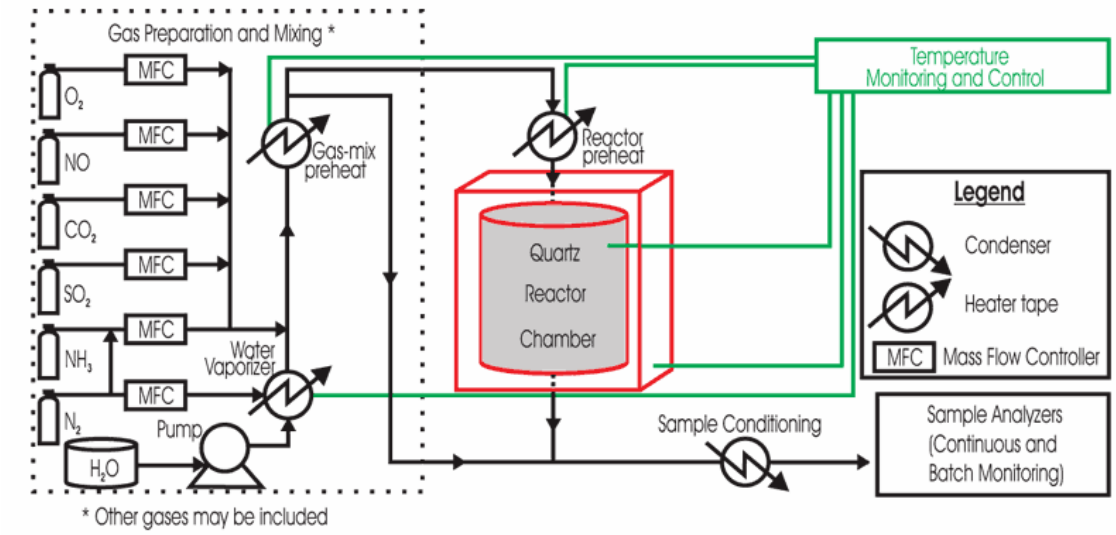

Figure 4. CTF gas-flow system.

For details concerning the validation and operation of the catalyst test facility, refer to the March 04 DOE Quarterly Report for the Calcium-Based Hg-Sorbents project conducted at Southern Research Institute [1] and a previous Quarterly Report on this project [2].

Results and Discussion

Catalyst Activity

Three different catalysts were tested this quarter. The three catalysts are different in their geometry, appearance, and composition, therefore any experiments performed for the oxidation of mercury would reflect these differences.

A test method was designed to establish a basis that would remove the bias of geometry, appearance, and formulation. Since SCR catalysts are designed for NO_x control, not mercury oxidation, the basis for the comparison of catalysts was equivalent NO_x reduction. The amount of each type of catalyst used was just enough to obtain a NO_x removal percentage of 70%, at 1:1 ammonia to NO_x molar ratio. In other words, the outlet NO_x concentration was 70% less than the inlet concentration for all catalyst types, with the appropriate amount of catalyst in the system. The flow rate, gas concentrations, gas temperature, and catalyst temperature were held constant for each test condition, and were continuously monitored and maintained throughout the test program.

At the beginning of each experiment, a blank quartz reactor was inserted into the gas stream to collect baseline data. After sufficient data were collected, the blank reactor was removed and replaced with the catalyst-packed reactor. During this time an inert stream of nitrogen replaced the ammonia flow required for a 1:1 ammonia to NO_x ratio. The catalyst temperature and gas temperature was allowed to reach a steady-state value of 700 °F, and the NO_x concentration was allowed to reach a steady-state value of 300 ppmv. This NO_x value was recorded as the inlet NO_x concentration. Following the inlet NO_x-concentration measurement, the ammonia was turned on. Then, the NO_x concentration was again allowed to reach steady-state, which was taken as the outlet NO_x concentration.

The NO_x removal efficiency was calculated using the inlet and outlet NO_x concentrations mentioned in the previous paragraph. This was determined by Equ. 2 below.

$$\eta_{\mathrm{NOx}} = \frac{NOx_{in} - NOx_{out}}{NOx_{in}} = \mathrm{NOx\ removal\ efficiency} \qquad (2)$$

If a value of 70% was calculated, the catalyst was retained for future mercury sorption and oxidation testing. If the value was greater or less than desired, the surface area was altered appropriately to change the measured NO_x-removal efficiency in the direction of 70% NO_x reduction. The catalyst was then retested by the aforementioned procedures. These steps were repeated for each catalyst type to ensure a consistent NO_x-removal efficiency basis of 70%.

The mathematical equations used to demonstrate the performance of SCR catalysts are listed below. The NO_x-removal efficiency was the independent variable in this test program. The test conditions used for the catalyst activity tests are listed in Table 1.

SCR Catalyst Performance Parameters

$$k = -AV * \ln(1 - \eta_{NOx} \cdot \alpha) = \text{catalyst activity coefficient}$$

$$AV = \frac{Q_{wet}}{SA} = \text{area velocity}\left(\frac{\text{m}}{\text{s}}\right)$$

$$\eta_{\text{NOx}} = \frac{NOx_{in} - NOx_{out}}{NOx_{in}} = \text{NOx removal efficiency}$$

$$\alpha = \text{stoichiometric ratio of ammonia to NO}_x$$

$$\text{Q}_{\text{wet}} = \text{Wet Volumetric Flow Rate}\left(\frac{\text{m}^3}{\text{s}}\right)$$

$$SA = \text{Catalyst Surface Area}\left(\text{m}^2\right)$$

Results from the NO_x-reduction experiments are listed in Table 2. The required catalyst surface area for the hybrid catalyst was less than the surface area required for the plate-type and honeycomb-type catalysts.

Table 1. $DeNO_x$ Test Conditions.

Test Condition	**Value**
Flow Rate (m^3/min)	0.005
Temperature (^oF)	700
Oxygen (%)	5
Carbon Dioxide (%)	15
Sulfur Dioxide (ppm)	500
Nitric Oxide (ppm)	300
Hydrogen Chloride (ppm)	2
Ammonia (ppm)	300
NH_3:NO_x Ratio	1

Table 2. SCR Catalyst Performance Parameters.

Catalyst Type	**NOx Removal Efficiency (%)**	**Surface Area (m^2)**	**Activity Coefficient (k)**
SCR Honeycomb-type	70	0.077	0.08
SCR Plate-type	70	0.076	0.08
SCR Hybrid-type	70	0.062[1]	0.10

Visual inspection of the catalysts showed that the hybrid catalyst was composed of a more porous material than the other types of catalysts. Also the geometry was such that it may have

[1] The SCR hybrid-type catalyst is irregular in shape; therefore an approximation of the geometric surface area was required. It is estimated that the approximate surface area is within +/- 20% of the actual surface area.

promoted small recirculation zones within the catalyst structure. However, the gas velocity was small for all tests, such that the flow was in the laminar regime for each of the SCR catalysts tested. Nevertheless, the hybrid catalyst had a higher activity coefficient, which resulted in a lower surface-area requirement to achieve the same NO_x-removal efficiency as the other catalyst types. The plate and honeycomb-type catalysts were composed of similar materials and simple geometries. Therefore, it was expected that the two catalysts would have similar activity coefficients, as was the case (see Table 2). These qualified and characterized catalyst samples were retained for future mercury sorption and oxidation testing.

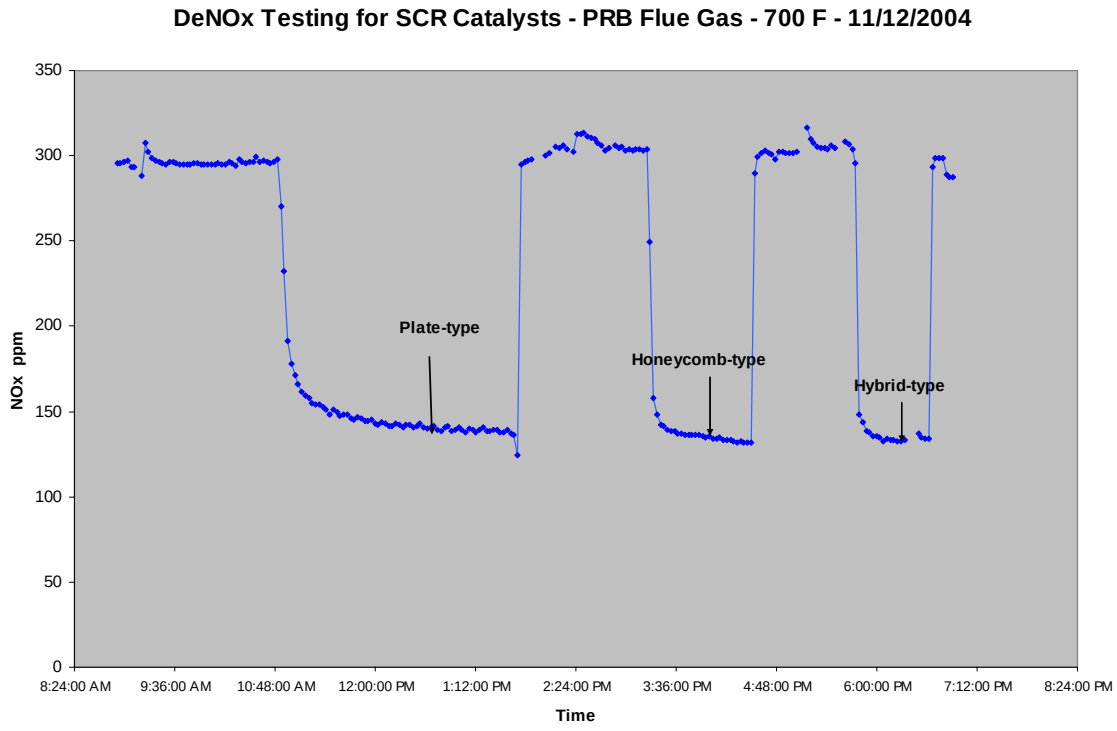

Figure 5. NO_x-concentration data for SCR catalysts.

Sorption Testing

The adsorption of mercury onto the surface of SCR catalysts is an important step in the mercury-oxidation process. The experiments described here are designed to yield an understanding of the mechanisms governing mercury adsorption on each of the three catalyst types. An explanation of the test methods is described.

Experiments were conducted to elucidate the adsorption of mercury onto different SCR catalyst types. Thus far two tests have been completed, one for the hybrid-type catalyst and one for the plate-type catalyst. There were a total of twelve experiments to be performed. The twelve tests were comprised of four inlet mercury concentration values and three-different catalyst types. The inlet mercury concentration was varied to determine its effect on the time required for the catalyst to reach steady-state. The collected data will be used to develop a mathematical relationship describing the adsorption kinetics of mercury onto the catalysts.

The adsorption experiments started with a blank reactor inserted in the furnace to collect baseline mercury concentration data at the reactor outlet. Once sufficient data were collected, the blank reactor was removed, and a reactor containing a single catalyst sample was inserted in its place. The sample was then exposed to flue gas containing mercury, overnight in the furnace. During that time, outlet mercury concentrations were measured and recorded. The overnight exposure period proved to be sufficient for the catalysts to reach steady state with respect to both oxidized and elemental mercury concentrations, with 10 $\mu g/m^3$ inlet mercury concentration. At the conclusion of the test period, the reactor containing the catalyst sample was removed from the furnace, and the blank reactor was reinserted in its place. Baseline data was again collected to ensure that the system did not drift during the test. These steps were repeated precisely for each test thus far, and will continue to be used for future testing.

Initial testing showed that the state of the catalyst sample could affect the adsorption of mercury onto the catalyst. If the catalyst had been exposed to mercury prior to the beginning of the experiment, then a steady-state concentration was achieved much faster than experiments using a sample that had not been exposed to mercury. Because of this phenomenon, the experiments performed during this stage of the project were required to use unexposed (fresh) catalyst samples. If a fresh sample was unavailable, then the exposed samples were regenerated by heating them to 750^oF for a 24-hour period. Inclusion of HCl gas at a concentration of 250 ppm, accelerated desorption of mercury from the exposed samples. Therefore, HCl was used each time the catalyst samples were regenerated.

During the initial test with each catalyst, the variability in the total mercury measurement was too great to determine a steady-state concentration value. Therefore, the length of time required to reach equilibrium was determined from the elemental mercury measurement. The variability in total mercury measurement was thought to be caused by the generation of SO_3 by the catalyst. One hypothesis is that SO_3 reacts with water vapor in the simulated flue gas and forms sulfuric acid (H_2SO_4). The acid condenses on the walls of the sampling system once the temperature drops below the acid dewpoint. The condensed acid acts as a scrubbing agent for the oxidized mercury portion of the simulated flue gas and collects this mercury on the walls of the sampling system. Further into the sampling system where the temperature falls below the water dewpoint, water will condense on the walls of the sampling system. The condensed water vapor will remove a portion of the remaining acid gases from the simulated flue gas. Again, the condensed acid act as a scrubbing agent, removing oxidized mercury. Once enough acid and water vapor has collected to form large droplets, some droplets dislodge from the walls of the

impinger and re-entrain the scrubbed mercury in the sample system resulting in a spike in the total-mercury concentration (See Figure 6). An additional issue associated with this phenomenon is that mercury measurements in the CTF occur on a semi-continuous basis, and instantaneous rises and falls in mercury concentration *are* recognized by the analyzer, but full recovery of the mass lost and gained during these instances is *not* achieved. Long-term averaging of the data has shown a loss of 6-7% in the total mercury concentration measurement. The loss is attributed to the initial sulfuric acid condensation mentioned earlier. SRI is working to resolve these issues for future tests.

The adsorption data from the hybrid-type catalyst is presented in Figure 6. The time required for the hybrid catalyst to reach steady state with respect to the measured mercury concentration in the flue gas was approximately 9 hours, with an inlet mercury concentration of 10 μg/m^3. The adsorption data from the plate-type catalyst is presented in Figure 7. The time required for the plate catalyst to reach steady state was approximately 7 hours (inlet Hg concentration was 10 μg/m^3), but the data for this experiment had much more variability than the data for the hybrid catalyst. The cause of this variability was unknown.

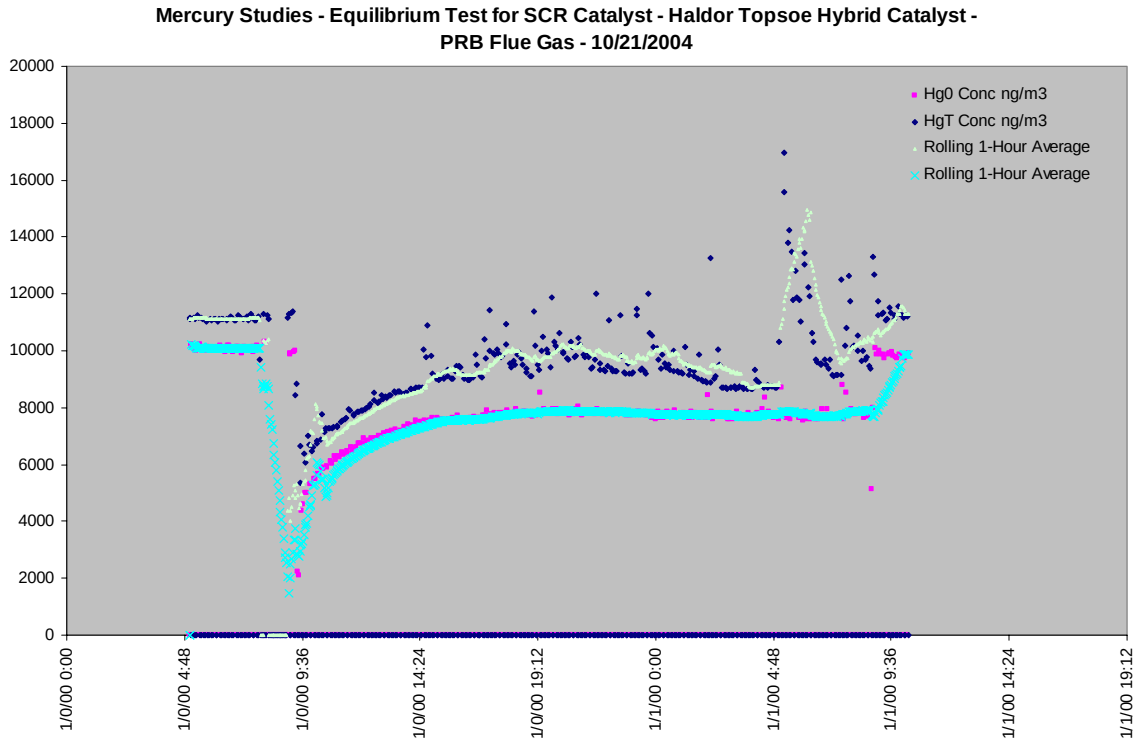

Figure 6. Equilibrium data for hybrid-type catalyst.

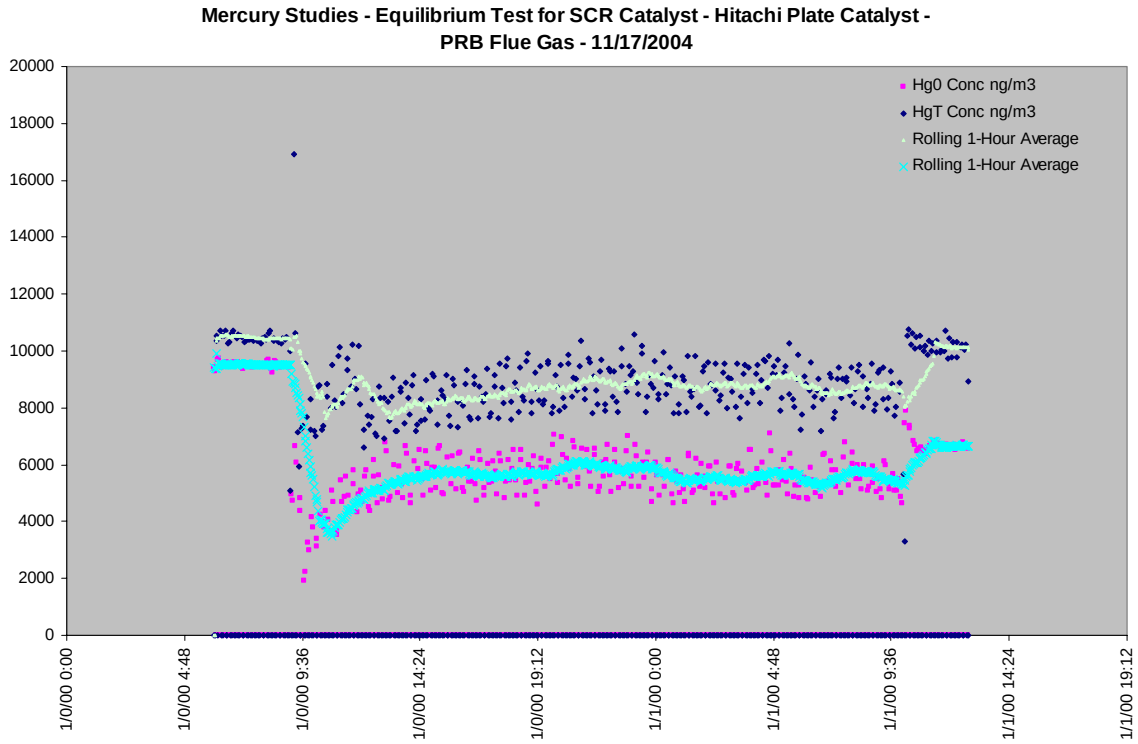

Figure 7. Equilibrium Data for Plate-type Catalyst

Conclusions

Initial tests have demonstrated the ability of SCR catalysts to promote mercury oxidation in coal-derived flue gas environments. In addition, a test method was developed for current and future experiments, to aid in determining the mechanisms governing mercury oxidation across SCR catalysts. Initial mercury-sorption testing has been performed on the three-different catalyst types. The time required to reach steady-state mercury adsorption across SCR catalysts in the CTF was found to be between 7 and 9 hours, for the established operating conditions for comparative testing of different SCR catalysts. There were issues with transient spikes, variability, and loss of oxidized mercury during the initial test with each of the catalyst types. Efforts will be made to solve these problems in subsequent quarters.

Future Work

Current testing of mercury adsorption on SCR catalysts will continue during the next quarter. The effects of different mercury and ammonia concentrations will be investigated, and the data will be used to elucidate the mechanisms governing the adsorption of mercury onto SCR catalysts. Also, each catalyst's potential to oxidize mercury and generate SO_3 will be investigated. Further, experiments will be conducted using different flue gases for specific coal types, varied levels of individual gas components (HCl, Hg, SO_3, and NH_3), and multiple gas temperatures. The data generated from these experiments will be used to develop a clear

understanding of mercury oxidation across SCR catalysts relative to full-scale coal-fired power plants.

References

1. Gale, T. K., “Catalyst Additives to Enhance Mercury Oxidation and Capture” Quarterly Report – DE-FC26-04NT41900 for period Mar. 1st through June. 30th, 2004.

2. Gale, T. K., “Mercury Control with Calcium-Based Sorbents and Oxidizing Agents” Quarterly Report – DE-PS26-02NT41183 for period Jan. 1st through Mar. 31st, 2004.

3. Gale, T. K. and Merritt, R. L., "Coal Blending, Ash Separation, Ash Re-Injection, Ash Conditioning, and Other Novel Approaches to Enhance Hg Uptake by Ash in Coal-Fired Electric Power Stations" *International Conference on Air Quality IV, Mercury, Trace Elements, and Particulate Matter*, Arlington, VA, September 22-24, 2003.

4. Gale, T. K., “Mercury Control with Calcium-Based Sorbents and Oxidizing Agents” DOE Mercury Control Technology R&D Program Review Meeting, Aug. 12-13, 2003.

5. Gale, T. K., “Mercury Control with Calcium-Based Sorbents and Oxidizing Agents” Quarterly Report – DE-PS26-02NT41183 first three Quarterly Reports in 2003.

6. Gale, T. K., “Effective Calcium-Based Sorbents for Mercury Control”, *EPRI-DOE-EPA-A&WMA Combined Utility Air Pollution Control Symposium: The MEGA Symposium*, Washington D.C., August 30-September 2 (2004).

7. Niksa, S., Helble, J. J., Fujiwara, N., “Kinetic Modeling of Homogeneous Mercury Oxidation: the importance of NO and H_2O in predicting oxidation in coal-derived systems”, *Environ. Sci. Technol.*, **35**: 3701-3706 (2001).

8. Niksa, S., Fujiwara, N., Fujita, Y., Tomura, K., Moritomi, H., Tuji, T., and Takasu, S., “A Mechanism for Mercury Oxidation in Coal-Derived Exhausts” *J. A&WMA* **52**: 894-901 (2001).

9. Senior, C. L., Chen, Z., and Sarofim, A. F., “Mercury Oxidation in Coal-Fired Utility Boilers: Validation of Gas-Phase Kinetic Models”, *A&WMA 95th Annual. Conference.*, Baltimore MD, (2002).

10. Smith, J. M., “Chemical Engineering Kinetics”, Copyright © 1981 by McGraw-Hill, Inc. ISBN 0-07-058710-8.